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PLANETARY PHYSICS

V: AN EXPANSION METHOD FOR CALCULATING ATOMIC PROPERTIES

II. Transition Probabilities

by M. Cohen and A. Dalgarno

Prepared under Contract No. NASw-840 *by*
GEOPHYSICS CORPORATION OF AMERICA
Bedford, Mass.
for

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ABSTRACT

An earlier expression for the expectation value of a single-electron operator which is stationary with respect to first-order variations of the state wave function has been generalized to the case of an off-diagonal matrix element connecting two different states. Explicit calculations are carried out of the probabilities of dipole transitions between configurations $1s^a\ 2s^b\ 2p^c$ and $1s^a\ 2s^{b-1}\ 2p^{c+1}$ for all members of the isoelectronic sequences from helium to neon and the importance of taking into account the mixing of degenerate configurations is demonstrated. The accuracy is at least comparable to that of the Hartree-Fock approximation and in cases where degeneracy is important it is much superior.

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An Expansion Method for Calculating Atomic Properties
II. Transition Probabilities

M. Cohen and A. Dalgarno

1. Introduction

An expression for the expectation value of an operator which is stationary with respect to first-order variations of the state wave function has been given by Dalgarno and Stewart (1956,1957) and it has been used as the basis of an expansion method for calculating the expectation values of single-electron operators (Dalgarno and Stewart 1957, 1958, 1960; Dalgarno, Davison and Stewart, 1960; Cohen and Dalgarno 1961, 1963a; Cohen, Dalgarno and McNamee, 1962). A generalization of the expression appropriate to the calculation of the probabilities of the $^2S - {}^2P^o$ transitions of the lithium isoelectronic sequence has been introduced by Cohen and Dalgarno (1963a) and, by a trivial extension, it may be applied to all off-diagonal matrix elements. The resulting expression leads to a simple expansion procedure, the accuracy of which should be comparable in many cases to that of the Hartree-Fock approximation.

2. Stationary expressions

Suppose $\phi_s^{(o)}$ is some approximate representation of the eigenfunction Φ_s of the sth state of an atomic system and $E_s^{(o)}$ is the approximate value of the eigenvalue E_s, such that

$$H \Phi_s = E_s \Phi_s \tag{1}$$

and

$$H_s \phi_s^{(o)} = E_s^{(o)} \phi_s^{(o)} \quad , \tag{2}$$

the latter equation defining the effective Hamiltonian H_s. Then if L is any function of the electron coordinates, the right-hand side of

$$\langle \Phi_s | L | \Phi_s \rangle = \langle \phi_s^{(o)} | L | \phi_s^{(o)} \rangle + 2 \langle \chi_s | H | \phi_s^{(o)} \rangle \tag{3}$$

where

$$(H_s - E_s^{(o)}) \chi_s + \left\{ L - \langle \phi_s^{(o)} | L | \phi_s^{(o)} \rangle \right\} \phi_s^{(o)} = 0 \tag{4}$$

such that $\langle \chi_s | \phi_s^{(o)} \rangle$ vanishes, is stationary with respect to first-order variations of $\phi_s^{(o)}$. Similarly, the right-hand side of

$$\langle \Phi_s | L | \Phi_t \rangle = \langle \phi_s^{(o)} | L | \phi_t^{(o)} \rangle + \langle \chi_s | H | \phi_t^{(o)} \rangle + \langle \chi_t | H | \phi_t^{(o)} \rangle, \tag{5}$$

where

$$(H_s - E_s^{(o)}) \chi_s + L \phi_t^{(o)} - \langle \phi_t^{(o)} | L | \phi_s^{(o)} \rangle \phi_s^{(o)}$$

$$= \left\{ \langle \phi_t^{(o)} | H_s - E_s^{(o)} | \chi_s \rangle + \langle \phi_t^{(o)} | L | \phi_t^{(o)} \rangle \right\} \phi_t^{(o)} \tag{6}$$

and

$$(H_t - E_t^{(o)})\chi_t + L\phi_s^{(o)} - \langle \phi_s^{(o)} | L | \phi_t^{(o)} \rangle \phi_t^{(o)}$$

$$= \left\{ \langle \phi_s^{(o)} | H_t - E_t^{(o)} | \chi_t \rangle + \langle \phi_s^{(o)} | L | \phi_s^{(o)} \rangle \right\} \phi_s^{(o)} \qquad (7)$$

such that

$$\langle \chi_s | \phi_s^{(o)} \rangle = \langle \chi_t | \phi_t^{(o)} \rangle = \langle \phi_s^{(o)} | \phi_t^{(o)} \rangle = 0 \qquad (8)$$

is stationary with respect to first-order variations of $\phi_s^{(o)}$ and $\phi_t^{(o)}$.

3. Transition probabilities

The calculation of the probability of a dipole transition between two quantum states described by wave functions ψ_a and ψ_b may be reduced to an evaluation of the absolute strength S(A,B) obtained by summing the component strengths

$$S(a,b) = \left| \left\langle \psi_a \right| \sum_{i=1} \underset{\sim}{r}_i \left| \psi_b \right\rangle \right|^2 \qquad (9)$$

where $\underset{\sim}{r}_i$ is the position vector of the ith electron of an N-electron system, over the projection quantum numbers of the initial and final states. With the assumption of Russell-Saunders (L-S) coupling, the absolute multiplet strength of a transition between a pair of configurations may be expressed in the form

$$S(L,L') = \mathcal{S}(M)\sigma^2 \quad , \qquad (10)$$

where $\mathcal{S}(M)$ is an algebraic factor depending upon the particular multiplet and σ^2 is a radial factor (cf. Condon and Shortley 1951). If only the change in the orbitals of the active electron is taken into account,

$$\sigma^2 = \frac{1}{4\ell_>^2 - 1} \left| \left\langle u|r|v \right\rangle \right|^2 \qquad (11)$$

where $\ell_>$ is the greater of the two azimuthal quantum numbers involved in the transition and u and v are the initial and final radial wave functions of the active electron. If the changes in the orbitals of the passive electrons are also taken into account, a more complicated formula is obtained which depends upon the configurations involved.

3.1 The $(1s2s)^3$ S - $(1s'2p)^3$P transition

The inverse of the nuclear charge Z provides a convenient expansion parameter for a perturbation solution of the Hartree-Fock radial equations (Dalgarno 1960, Cohen and Dalgarno 1961, Linderberg 1961). Choosing a set of units in which the distance scale is Z atomic units and the energy scale is Z^2 atomic units, defining the radial Hamiltonian

$$H_k = -\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{1}{r} + \frac{k(k+1)}{2r^2} \tag{12}$$

and the radial integrals

$$Y^k(u,v) = r^{-(k+1)} \int_o^r u(s)v(s)s^{k+2}\,ds + r^k \int_r^\infty u(s)v(s)s^{1-k}\,ds, \tag{13}$$

the Hartree-Fock equations for the ^{3}S configuration are

$$H_o|1s\rangle + Y^o(2s,2s)|1s\rangle - Y^o(1s,2s)|2s\rangle = \epsilon(1s)|1s\rangle \tag{14}$$

and

$$H_o|2s\rangle + Y^o(1s,1s)|2s\rangle - Y^o(1s,2s)|1s\rangle = \epsilon(2s)|2s\rangle\ , \tag{15}$$

and for the ^{3}P configuration are

$$H_o|1s'\rangle + Y^o(2p,2p)|1s'\rangle - \frac{1}{3}Y^1(1s',2p)|2p\rangle = \epsilon(1s')|1s'\rangle \tag{16}$$

and

$$H_1|2p\rangle + Y^o(1s',1s')|2p\rangle - \frac{1}{3}Y^1(1s',2p)|1s\ \rangle = \epsilon(2p)|2p\rangle\ . \tag{17}$$

Expanding according to

$$|n\ell\rangle = |n\ell\rangle_0 + |n\ell\rangle_1 + |n\ell\rangle_2 + \ldots , \tag{18}$$

$$\epsilon(n\ell) = \epsilon_0(n\ell) + \epsilon_1(n\ell) + \epsilon_2(n\ell) + \ldots , \tag{19}$$

$$Y^k(n\ell,n'\ell') = Y_1^k(n\ell,n'\ell') + Y_2^k(n\ell,n'\ell') + \ldots , \tag{20}$$

the zero-order equations derived from (14) - (17) are simply the hydrogenic equations, the solutions of which are the hydrogen eigenfunctions. If we replace $|1s\rangle$ by u, $|2s\rangle$ by v, and $|2p\rangle$ by w, the first-order equations are

$$\left(H_o - \epsilon_o(1s)\right) u_1 + Y_1^o(2s,2s)u_o - Y_1^o(1s,2s)v_o = \epsilon_1(1s)u_o , \tag{21}$$

$$\left(H_o - \epsilon_o(2s)\right) v_1 + Y_1^o(1s,1s)v_o - Y_1^o(1s,2s)u_o = \epsilon_1(2s)v_o , \tag{22}$$

$$\left(H_o - \epsilon_o(1s')\right) u_1' + Y_1^o(2p,2p)u_o - \frac{1}{3} Y_1^1(1s,2p)w_o = \epsilon_1(1s')u_o , \tag{23}$$

and

$$\left(H_1 - \epsilon_o(2p)\right) w_1 + Y_1^o(1s,1s)w_o - \frac{1}{3} Y_1^1(1s,2p)u_o = \epsilon_1(2p)w_o . \tag{24}$$

The operators $Y_1^k(n\ell,n'\ell')$ appearing in these equations have been given explicitly by Cohen (1963).

Now introduce well-behaved functions V and W such that

$$\left(H_o - \epsilon_o(2s)\right) V + r\, w_o - \langle w_o|r|v_o\rangle\, v_o = 0 \tag{25}$$

and

$$\left(H_1 - \epsilon_o(2p)\right) W + r\, v_o - \langle v_o|r|w_o\rangle\, w_o = 0 \quad . \tag{26}$$

Without loss of generality we require that

$$\langle V|v_o\rangle = \langle W|w_o\rangle = 0 \quad . \tag{27}$$

Then,

$$\langle v_o|r|w_o\rangle = -3\sqrt{3} \ , \tag{28}$$

$$V = -\frac{1}{2\sqrt{6}}\,(12 - 6r - 6r^2 + r^3)\exp(-\tfrac{1}{2}r) \ , \tag{29}$$

and

$$W = -\frac{1}{2\sqrt{2}}\,(30r - r^3)\exp(-\tfrac{1}{2}r) \quad . \tag{30}$$

We can now calculate $\langle v|r|w\rangle$ exactly to first order. Thus, the zero-order contribution is given by (28) and the first-order contribution may after some manipulation be written

$$\begin{aligned}&\{\langle v_1|r|w_o\rangle + \langle v_o|r|w_1\rangle - \langle v_o|r|w_o\rangle\,[\langle v_1|v_o\rangle + \langle w_1|w_o\rangle]\}\\ &= \{\langle V|Y_1{}^o(1s,1s)|v_o\rangle - \langle V|Y_1{}^o(1s,2s)|u_o\rangle\\ &\quad + \langle W|Y_1{}^o(1s,1s)|w_o\rangle - \tfrac{1}{3}\langle W|Y_1{}^1(1s,2p)|u_o\rangle\} \quad .\end{aligned} \tag{31}$$

The matrix elements appearing in (31) occur (in different combinations) in all calculations involving a 2s - 2p transition and they are listed in Appendix A. From them we obtain

$$\langle v|r|w\rangle = -\frac{3\sqrt{3}}{Z} - \frac{46{,}640\sqrt{3}}{3^9 Z^2} + O(Z^{-3}) \ , \tag{32}$$

so that corresponding to (11)

$$\sigma^2 = \left(\frac{3}{Z} + \frac{46{,}640}{3^9 Z^2}\right)^2 \quad . \tag{33}$$

Application of the screening approximation (Dalgarno and Stewart 1960), which makes some allowance for higher order terms, yields

$$\sigma^2 = \frac{9}{(Z - 0.790)^2} \tag{34}$$

If we take into account the contribution of the passive electron,

$$\sigma^2 = \frac{1}{3}\left[\langle u|u'\rangle\langle v|r|w\rangle - \langle v|u'\rangle\langle u|r|w\rangle\right]^2. \tag{35}$$

Now

$$\langle u|u'\rangle = 1 + O(Z^{-2}) \tag{36}$$

and

$$\langle v|u'\rangle = \left[\langle v_1|u_o\rangle + \langle v_o|u_1'\rangle\right]Z^{-1} + O(Z^{-2}), \tag{37}$$

so that (31) must be modified by subtracting a quantity Δ where

$$\Delta = \left[\langle v_1|u_o\rangle + \langle v_o|u_1'\rangle\right]\langle u_o|r|w_o\rangle. \tag{38}$$

We may eliminate the first-order functions v_1 and u_1' from (38). Thus, $\langle v|u\rangle = 0$ to all orders and in particular

$$\langle v_1|u_o\rangle + \langle v_o|u_1\rangle = 0 \tag{39}$$

so that

$$\Delta = \left[\langle v_o|u_1'\rangle - \langle v_o|u_1\rangle\right]\langle u_o|r|w_o\rangle. \tag{40}$$

From (21),

$$\langle v_o|H_o - \epsilon_o(1s)|u_1\rangle = \langle v_o|Y_1^o(1s,2s)|v_o\rangle - \langle v_o|Y_1^o(2s,2s)|u_o\rangle, \tag{41}$$

the right-hand side of which is identically zero. The left-hand side may be written

$$\langle u_1 | H_o - \epsilon_o(2s) | v_o \rangle + [\epsilon_o(2s) - \epsilon_o(1s)] \langle u_1 | v_o \rangle$$

$$= \frac{3}{8} \langle v_o | u_1 \rangle \quad , \tag{42}$$

and hence $\langle v_o | u_1 \rangle = 0$. Similarly,

$$\frac{3}{8} \langle v_o | u_1' \rangle = \frac{1}{3} \langle v_o | Y_1^1(1s,2p) | w_o \rangle - \langle v_o | Y_1^o(2p,2p) | u_o \rangle \tag{43}$$

which may be evaluated from the matrix elements given in Appendix A. Using

$$\langle u_o | r | w_o \rangle = \frac{2^7\sqrt{6}}{3^5} \quad , \tag{44}$$

it follows that

$$\Delta = -\frac{2^{19}\sqrt{3}}{3^9 \cdot 5^5} \quad , \tag{45}$$

and σ^2 is given correct to first order by

$$\sigma^2 = \left(\frac{3}{Z} + \frac{145,225,712}{3^9 \cdot 5^5 \cdot Z^2} \right)^2 \quad . \tag{46}$$

Application of the screening approximation yields

$$\sigma^2 = \frac{9}{(Z - 0.787)^2} \quad , \tag{47}$$

comparison with (34) suggesting that the lack of orthogonality of the initial 2s and the final 1s orbital has a negligible effect even for helium.

3.2 The $(1s2s)^1S$ - $(1s'2p)^1P$ transition

The Hartree-Fock equations for the singlet configurations have been critically discussed by Sharma and Coulson (1962). They lead to the first-order equations

$$\left(H_o - \epsilon_o(1s)\right)u_1 + Y_1^o(2s,2s)u_o + Y_1^o(1s,2s)v_o$$

$$= \epsilon_1(1s)u_o + \left\langle v_o|Y_1^o(1s,2s)|v_o\right\rangle v_o \quad , \tag{48}$$

$$\left(H_o - \epsilon_o(2s)\right)v_1 + Y_1^o(1s,1s)v_o + Y_1^o(1s,2s)u_o$$

$$= \epsilon_1(2s)v_o + \left\langle u_o|Y_1^o(1s,2s)|u_o\right\rangle u_o \quad , \tag{49}$$

for the ^1S state and

$$\left(H_o - \epsilon_o(1s)\right)u_1' + Y_1^o(2p,2p)u_o + \frac{1}{3}\,Y_1^1(1s,2p)w_o = \epsilon_1(1s')u_o \quad , \tag{50}$$

$$\left(H_1 - \epsilon_o(2p)\right)w_1 + Y_1^o(1s,1s)w_o + \frac{1}{3}\,Y_1^1(1s,2p)u_o = \epsilon_1(2p)w_o \quad , \tag{51}$$

for the ^1P state.

The zero-order term is again $\left\langle v_o|r|w_o\right\rangle$ as for the triplet transition while the first-order term is

$$\left\{\left\langle V|Y_1^o(1s,1s)|v_o\right\rangle + \left\langle V|Y_1^o(1s,2s)|u_o\right\rangle - \left\langle u_o|Y_1^o(1s,2s)|u_o\right\rangle\left\langle V|u_o\right\rangle\right.$$

$$\left. + \left\langle W|Y_1^o(1s,1s)|w_o\right\rangle + \frac{1}{3}\left\langle W|Y_1^1(1s,2p)|u_o\right\rangle\right\} , \tag{52}$$

yielding the exact result

$$\langle v|r|w\rangle = -\frac{3\sqrt{3}}{Z} - \frac{155,713,968\sqrt{3}}{3^9 \cdot 7^4 \cdot Z^2} + O(Z^{-3}) \tag{53}$$

which on application of the screening approximation yields

$$\sigma^2 = \frac{9}{(Z - 1.098)^2} \quad . \tag{54}$$

The complete expression for σ^2 which allows for the change of the 1s orbital is

$$\sigma^2 = \frac{1}{3}\left[\langle u|u'\rangle\langle v|r|w\rangle + \langle v|u'\rangle\langle u|r|w\rangle\right]^2 \quad . \tag{55}$$

By an analysis similar to that used for the triplet case, it may be shown that

$$\frac{3}{8}\langle v_o|u_1\rangle = -\langle v_o|Y_1^o(1s,2s)|v_o\rangle \quad , \tag{56}$$

$$\frac{3}{8}\langle v_o|u_1'\rangle = -\langle v_o|Y_1^o(2p,2p)|u_o\rangle - \frac{1}{3}\langle v_o|Y_1^1(1s,2p)|w_o\rangle \, , \tag{57}$$

and

$$\Delta = \frac{2^{19}\sqrt{3}}{3^8 \cdot 5^5} \quad . \tag{58}$$

Thus to first order, (55) is given by

$$\sigma^2 = \left(\frac{3}{Z} + \frac{482,829,703,536}{3^9 \cdot 5^5 \cdot 7^4 \cdot Z^2}\right)^2 \, , \tag{59}$$

and (54) is replaced by the improved formula

$$\sigma^2 = \frac{9}{(Z - 1.090)^2} \quad , \tag{60}$$

the effect of the passive electron again being negligible.

3.3 The $(1s^2\ 2s^a\ 2p^b)SL$ - $(1s'^2\ 2s'^{a-1}\ 2p'^{b+1})SL'$ transitions

The Hartree-Fock equations for the configuration $1s^2\ 2s^a(2p^b\ S_1\ L)SL$ are

$$\left(H_o - \epsilon(1s)\right)u + Y^o(1s,1s)u + a\left[Y^o(2s,2s)u - \frac{1}{2}\,Y^o(1s,2s)v\right]$$

$$+ b\left[Y^o(2p,2p)u - \frac{1}{6}\,Y^1(1s,2p)w\right] = \frac{1}{2}\,\delta_{a1}\,\epsilon(1s,2s)v\ , \qquad (61)$$

$$\left(H_o - \epsilon(2s)\right)v + (a-1)Y^o(2s,2s)v + 2\left[Y^o(1s,1s)v - \frac{1}{2}\,Y^o(1s,2s)u\right]$$

$$+ b\left[Y^o(2p,2p)v - \frac{1}{6}\,Y^1(2s,2p)w\right] + \frac{1}{a}\,\delta_{a1}\lambda Y^1(2s,2p)w$$

$$= \delta_{a1}\epsilon(1s,2s)u\ , \qquad (62)$$

and

$$H_1 - \epsilon_o(2p)\,w + (b-1)\left[Y^o(2p,2p)w - \frac{2}{25}\,Y^2(2p,2p)w\right]$$

$$+ 2\left[Y^o(1s,1s)w - \frac{1}{6}\,Y^1(1s,2p)u\right] + a\left[Y^o(2s,2s)w - \frac{1}{6}\,Y^1(2s,2p)v\right]$$

$$+ \frac{1}{b}\left[\delta_{a1}\lambda Y^1(2s,2p)v + \frac{6}{25}\,\mu Y^2(2p,2p)w\right] = 0\ , \qquad (63)$$

where

$$\lambda = \frac{1}{3}\left[S_1(S_1+1) - S(S+1) + \frac{3}{4}\right] \qquad (64)$$

and $\mu = \mu(b,S_1,L)$ is given in Table 1.

The explicit expression for the off-diagonal parameter

$$\epsilon(1s,2s) = 2\lambda\left\langle v\middle|Y^1(1s,2p)\middle|w\right\rangle - \left\langle v\middle|Y^o(1s,2s)\middle|v\right\rangle \qquad (65)$$

follows from (61) and (62).

Similar equations may be written down for the configuration $1s'^2\ 2s'^{a-1}\ (2p'^{b+1}\ S_1'\ L')\ SL'$ and after considerable manipulation we obtain for the first order contribution to $\left\langle v\middle|r\middle|w\right\rangle$

$$\left\{\langle v_1|r|w_o\rangle + \langle v_o|r|w_1\rangle - \langle v_o|r|w_o\rangle[\langle v_1|v_o\rangle + \langle w_1|w_o\rangle]\right\}$$

$$= \left\{2[\langle V|Y_1^o(1s,1s)|v_o\rangle - \tfrac{1}{2}\langle V|Y_1^o(1s,2s)|u_o + \langle W|Y_1^o(1s,1s)|w_o\rangle\right.$$

$$- \tfrac{1}{6}\langle W|Y_1^1(1s,2p)|u_o\rangle] + (a-1)\ [\langle V|Y_1^o(2s,2s)|v_o\rangle$$

$$+ \langle W|Y_1^o(2s,2s)|w_o\rangle - \tfrac{1}{6}\langle W|Y_1^1(2s,2p)|v_o\rangle]$$

$$+ b\ [\langle V|Y_1^o(2p,2p)|v_o\rangle - \tfrac{1}{6}\langle V|Y_1^1(2s,2p)|w_o\rangle$$

$$+ \langle W|Y_1^o(2p,2p)|w_o\rangle - \tfrac{2}{25}\langle W|Y_1^2(2p,2p)|w_o\rangle]$$

$$+ \delta_{a1}\ [\lambda\langle V|Y_1^1(2s,2p)|w_o\rangle - \epsilon_1(1s,2s)\langle V|u_o\rangle]$$

$$+ \frac{1}{(b+1)}\ [\delta_{a2}\ \lambda'\langle W|Y_1^1(2s,2p)|v_o\rangle$$

$$\left. + \tfrac{6}{25}\mu'\langle W|Y_1^2(2p,2p)|w_o\rangle]\right\} \quad , \tag{66}$$

where

$$\lambda'(S_1',S) = \lambda(S_1,S) \tag{67}$$

and

$$\mu'(b+1,S_1',L) = \mu(b,S_1,L) \tag{68}$$

By evaluating (66) with the values of a, b, λ, λ', and μ' listed in Table 2, we may obtain the one-electron transition integral $\langle v|r|w\rangle$ correct to first order in the form

$$\langle v|r|w\rangle = -3\lambda/3\left(\frac{1}{Z} + \frac{\tau}{Z^2}\right) \quad , \tag{69}$$

which leads to

$$\sigma^2 = \frac{9}{(Z-\tau)^2} \quad . \tag{70}$$

Values of τ, correct to three significant figures, are given in Table 3 for all permitted L-shell 2s - 2p transitions.

The expression for σ^2 which allows for the changes in the orbitals of the passive electron depends upon the particular transition, but it may be shown that to first order in Z^{-1} it reduces to a subtraction of the correction term

$$\Delta = \left[\langle v_o|u_1'\rangle - \langle v_o|u_1\rangle\right]\langle u_o|r|w_o\rangle , \tag{71}$$

which may be written alternatively as

$$\begin{aligned}\Delta = \frac{8}{3}\langle u_o|r|w_o\rangle\Big[&\frac{1}{2}\langle v_o|Y_1^o(1s,2s)|v_o\rangle \\ &- \langle w_o|Y_1^o(1s,2s)|w_o\rangle + \frac{1}{6}\langle v_o|Y_1^1(1s,2p)|w_o\rangle \\ &+ \frac{1}{2}\delta_{a2}\,\epsilon_1(1s',2s') - \frac{1}{2}\delta_{a1}\,\epsilon_1(1s,2s)\Big] ,\end{aligned} \tag{72}$$

where

$$\epsilon_1(1s,2s) = 2\lambda\langle v_o|Y_1^1(1s,2p)|w_o\rangle - \langle v_o|Y_1^o(1s,2s)|v_o\rangle \tag{73}$$

and

$$\epsilon_1(1s',2s') = 2\lambda'\langle v_o|Y_1^1(1s,2p)|w_o\rangle - \langle v_o|Y_1^o(1s,2s)|v_o\rangle . \tag{74}$$

Values of Δ and of the modified screening constants τ and τ', such that

$$\sigma^2 = \frac{9}{(Z - \tau')^2} \tag{75}$$

are given in Table 3. A comparison of τ and τ' suggests that the usual approximation of ignoring the passive electrons is entirely justified for 2s - 2p transitions.

3.4 Results of single-configuration calculations

We have calculated only the two leading terms of (70) and its accuracy as a representation of the entire series expansion of σ^2 is uncertain, though our earlier results for the lithium sequence (Cohen and Dalgarno 1963) were very encouraging. Fortunately, detailed calculations of 2s - 2p transition probabilities in neutral and ionized oxygen and nitrogen have been carried out using analytic Hartree-Fock wave-functions (Roothan and Kelly 1963) and a full comparison is presented in Table 4. The over-all agreement is extremely good and the error of (70) does not exceed 15 percent even for the case of neutral nitrogen. Since our method is an exact representation of the Hartree-Fock results in the limit of infinite nuclear charge, the rapid increase in the accuracy of (70) as Z increases is a confirmation of the precision of the detailed numerical work of Roothan and Kelly. The accuracy of (70) for neutral species is confirmed also for carbon, which has been the subject of a variational treatment by Bolotin, Levinson and Levin (1956).

That (70) should remain accurate even for neutral systems is unexpected and it would be unduly optimistic to expect similar accuracy for other transitions. However, it suggests that an investigation using the expansion method of the errors arising from the single-configuration (Hartree-Fock) approximation will have more than qualitative significance.

3.5 The two-configuration approximation

The importance of the mixing of degenerate configurations in predicting the ratios of the term splittings in a configuration has been pointed out by Layzer (1959) and it has been noted by Linderberg and Shull (1960) that the degeneracy gives rise to a correlation energy which increases with the nuclear charge. Cohen and Dalgarno (1963b) have further shown that because it ignores the degeneracies, the Hartree-Fock approximation is inadequate for predicting the isotope shifts for certain spectral lines.

The degenerate configurations which occur in open L-shells are characterized by $1s^2\ 2s^2\ 2p^b$ and $1s^2\ 2p^{b+2}$ and the single configuration wave function $\psi_1(1s^2\ 2s^2\ 2p^b\ ;\ SL)$ must in the limit of infinite nuclear charge be replaced by

$$\begin{aligned}\psi(SL) &= \alpha\psi_1(1s^2 2s^2 2p^b;SL) + \beta\psi_2(1s^2 2p^{b+2};SL) \\ &= \alpha\psi_1 + \beta\psi_2\ , \quad \text{say,} \end{aligned} \tag{76}$$

where α and β are chosen so that the matrix of the Hamiltonian is diagonal. If the final configuration $(1s^2 2s^2 2p^{b+1})SL'$ is denoted by the number 3, the expression (10) for the multiplet strength

$$S(1;3) = \mathcal{A}(M)\sigma^2(1;3) \tag{77}$$

is replaced by

$$S(1,2;3) = \mathcal{A}(M)\left[\alpha\sigma(1;3) + \beta\gamma\sigma(2;3)\right]^2\ , \tag{78}$$

where $\zeta(M)$ and γ are algebraic factors which depend upon the configurations and the multiplet.

The magnitudes of α and β have been listed by Cohen and Dalgarno (1963b) and the magnitudes of γ may be derived from formulae listed by Rohrlich (1959). Because the relative sign of α and $\beta\gamma$ is significant in (78), it was necessary to repeat their analyses, taking care to ensure a consistent choice of phases. We adopted the phase conventions of Racah (1942, 1943) and followed his procedures.

The final results for the absolute multiplet strengths of all L-shell transitions involving the one-electron 2s-2p jump are collected in Table 5 where $\zeta(M)$, α, β, γ, τ'_α and τ'_β are listed. The absolute multiplet strengths are given in terms of them by the formula

$$S(SL;SL') = \zeta(M)\left[\frac{3\alpha}{(Z - \tau'_\alpha)} + \frac{3\beta\gamma}{(Z - \tau'_\beta)}\right]^2 . \qquad (79)$$

The effect of the mixing of degenerate configurations is illustrated in Table 6 where the relative strengths of the multiplets arising from transitions between a pair of configurations are compared with those obtained from the (Hartree-Fock) single-configuration approximation, in which the distortion of the passive electrons is ignored. Similar but less extensive results have been obtained by Iutsis and Kavetskis (1951), by Bolotin and Iutsis (1953) and by Bolotin, Levinson and Levin (1956), who carried out detailed variational calculations for individual systems.

It is clear from Table 6 that where degeneracy occurs, the Hartree-Fock approximation is inadequate for the prediction of relative multiplet strengths.

Table 1

Values of $\mu(b, S_1, L)$, Eq. (63)

State	^4S	^3P	^2D	^1D	^2P	^1S
$\mu(2, S_1, L)$ $\mu(4, S_1, L)$	-	-1	-	1	-	4
$\mu(3, S_1, L)$	-3	-	0	-	2	-

Table 2

Parameters of the L-shell transitions Eq. (66)

N	Configurations* a	b	Transition	6λ	$6\lambda'$	μ'
3	1	0	$^2S - ^2P$	0	0	0
4	2	0	$^1S - ^1P$	0	3	0
	1	1	$^3P - ^3P$	-1	0	-1
			$^1P - ^1D$	3	0	1
			$^1P - ^1S$	3	0	4
5	2	1	$^2P - ^2D$	0	0	1
			$^2P - ^2P$	0	4	-1
			$^2P - ^2S$	0	0	4
	1	2	$^4P - ^4S$	-2	0	-3
			$^2D - ^2D$	0	0	0
			$^2D - ^2P$	0	0	2
			$^2P - ^2D$	4	0	0
			$^2P - ^2P$	4	0	2
			$^2S - ^2P$	0	0	2
6	2	2	$^3P - ^3D$	0	-1	0
			$^3P - ^3P$	0	-1	2
			$^3P - ^3S$	0	5	-3
			$^1D - ^1D$	0	3	0
			$^1D - ^1P$	0	3	2
			$^1S - ^1P$	0	3	2

* $1s^2 2s^a 2p^b$, $1s^2 2s^{a-1} 2p^{b+1}$

Table 2 (Continued)

N	Configurations* a	b	Transition	6λ	6λ'	μ'
6	1	3	$^3D - {}^3P$	-1	0	-1
			$^3P - {}^3P$	-1	0	-1
			$^3S - {}^3P$	5	0	-1
			$^1D - {}^1D$	3	0	1
			$^1P - {}^1D$	3	0	1
			$^1P - {}^1S$	3	0	4
7	2	3	$^4S - {}^4P$	0	-2	-1
			$^2D - {}^2D$	0	0	1
			$^2D - {}^2P$	0	4	-1
			$^2P - {}^2D$	0	0	1
			$^2P - {}^2P$	0	4	-1
			$^2P - {}^2S$	0	0	4
	1	4	$^2D - {}^2P$	0	0	0
			$^2P - {}^2P$	4	0	0
			$^2S - {}^2P$	0	0	0
8	2	4	$^3P - {}^3P$	0	-1	0
			$^1D - {}^1P$	0	3	0
			$^1S - {}^1P$	0	3	0
	1	5	$^1P - {}^1S$	3	0	0
9	2	5	$^2P - {}^2S$	0	0	0

* $1s^2 2s^a 2p^b$, $1s^2 2s^{a-1} 2p^{b+1}$

Table 3

Screening parameters for the L-shell transitions. Eqs. (70), (72) and (75)

N	Configurations a	Configurations b	Transition	$-\Delta$	τ	τ'
3	1	0	$^2S - ^2P$	0.01279	1.699	1.694
4	2	0	$^1S - ^1P$	0.06819	1.995	1.973
	1	1	$^3P - ^3P$	0.02557	2.074	2.066
			$^1P - ^1D$	-0.02557	2.157	2.165
			$^1P - ^1S$	-0.02557	2.228	2.237
5	2	1	$^2P - ^2D$	0.02983	2.466	2.456
			$^2P - ^2P$	0.08098	2.392	2.366
			$^2P - ^2S$	0.02983	2.537	2.527
	1	2	$^4P - ^4S$	0.03836	2.450	2.437
			$^2D - ^2D$	0.01279	2.515	2.511
			$^2D - ^2P$	0.01279	2.547	2.543
			$^2P - ^2D$	-0.03836	2.550	2.563
			$^2P - ^2P$	-0.03836	2.582	2.595
			$^2S - ^2P$	0.01279	2.547	2.543
6	2	2	$^3P - ^3D$	0.01705	2.854	2.849
			$^3P - ^3P$	0.01705	2.886	2.880
			$^3P - ^3S$	0.09376	2.781	2.750
			$^1D - ^1D$	0.06819	2.837	2.815
			$^1D - ^1P$	0.06819	2.869	2.846
			$^1S - ^1P$	0.06819	2.869	2.846

Table 3 (Continued)

N	Configurations a	b	Transition	-△	τ	τ°
6	1	3	$^3D - {}^3P$	0.02557	2.903	2.894
			$^3P - {}^3P$	0.02557	2.903	2.894
			$^3S - {}^3P$	-0.05114	2.955	2.972
			$^1D - {}^1D$	-0.02557	2.962	2.970
			$^1P - {}^1D$	-0.02557	2.962	2.970
			$^1P - {}^1S$	-0.02557	2.997	3.006
7	2	3	$^4S - {}^4P$	0.00426	3.253	3.251
			$^2D - {}^2D$	0.02983	3.270	3.260
			$^2D - {}^2P$	0.08098	3.234	3.207
			$^2P - {}^2D$	0.02983	3.270	3.260
			$^2P - {}^2P$	0.08098	3.234	3.207
			$^2P - {}^2S$	0.02983	3.306	3.296
	1	4	$^2D - {}^2P$	0.01279	3.332	3.327
			$^2P - {}^2P$	-0.03836	3.367	3.379
			$^2S - {}^2P$	0.01279	3.332	3.327
8	2	4	$^3P - {}^3P$	0.01705	3.669	3.663
			$^1D - {}^1P$	0.06819	3.659	3.636
			$^1S - {}^1P$	0.06819	3.659	3.636
	1	5	$^1P - {}^1S$	-0.02557	3.766	3.775
9	2	5	$^2P - {}^2S$	0.02983	4.075	4.065

Table 4

Comparison with Hartree-Fock values of σ^2 for L-shell 2s-2p transitions in neutral and ionized oxygen and nitrogen

Ion	a	b	Transition	Hartree-Fock	Eq. (70)
O	2	4	$^3P - {}^3P$	0.449	0.480
			$^1D - {}^1P$	0.450	0.478
			$^1S - {}^1P$	0.448	0.478
	1	5	$^1P - {}^1S$	0.454	0.502
O^+	2	3	$^4S - {}^4P$	0.388	0.399
			$^2D - {}^2D$	0.390	0.402
			$^2D - {}^2P$	0.390	0.396
			$^2P - {}^2D$	0.389	0.402
			$^2P - {}^2P$	0.389	0.396
			$^2P - {}^2S$	0.392	0.408
	1	4	$^2D - {}^2P$	0.386	0.413
			$^2P - {}^2P$	0.404	0.425
			$^2S - {}^2P$	0.385	0.413
O^{+2}	2	2	$^3P - {}^3D$	0.336	0.340
			$^3P - {}^3P$	0.339	0.344
			$^3P - {}^3S$	0.334	0.330
			$^1D - {}^1D$	0.338	0.338
			$^1D - {}^1P$	0.340	0.342
			$^1S - {}^1P$	0.340	0.342
	1	3	$^3D - {}^3P$	0.334	0.346
			$^3P - {}^3P$	0.334	0.346
			$^3S - {}^3P$	0.355	0.354
			$^1D - {}^1D$	0.348	0.355
			$^1P - {}^1D$	0.347	0.355
			$^1P - {}^1S$	0.350	0.360
O^{+3}	2	1	$^2P - {}^2D$	0.294	0.294
			$^2P - {}^2P$	0.292	0.286
			$^2P - {}^2S$	0.300	0.302

Table 4 (Continued)

Ion	a	b	Transition	Hartree-Fock	Eq. (70)
	1	2	$^4P - {}^4S$	0.288	0.292
			$^2D - {}^2D$	0.295	0.299
			$^2D - {}^2P$	0.297	0.303
			$^2P - {}^2D$	0.305	0.303
			$^2P - {}^2P$	0.308	0.307
			$^2S - {}^2P$	0.297	0.303
O^{+4}	2	0	$^1S - {}^1P$	0.256	0.250
	1	1	$^3P - {}^3P$	0.256	0.256
			$^1P - {}^1D$	0.266	0.264
			$^1P - {}^1S$	0.271	0.270
O^{+5}	1	0	$^2S - {}^2P$	0.228	0.227
N	2	3	$^4S - {}^4P$	0.610	0.641
			$^2D - {}^2D$	0.613	0.647
			$^2D - {}^2P$	0.614	0.635
			$^2P - {}^2D$	0.610	0.647
			$^2P - {}^2P$	0.611	0.635
			$^2P - {}^2S$	0.614	0.660
	1	4	$^2D - {}^2P$	0.594	0.669
			$^2P - {}^2P$	0.626	0.682
			$^2S - {}^2P$	0.590	0.669
N^+	2	2	$^3P - {}^3D$	0.515	0.524
			$^3P - {}^3P$	0.519	0.532
			$^3P - {}^3S$	0.514	0.506
			$^1D - {}^1D$	0.518	0.519
			$^1D - {}^1P$	0.523	0.527
			$^1S - {}^1P$	0.521	0.527
	1	3	$^3D - {}^3P$	0.506	0.536
			$^3P - {}^3P$	0.505	0.536
			$^3S - {}^3P$	0.548	0.550
			$^1D - {}^1D$	0.532	0.552
			$^1P - {}^1D$	0.529	0.552
			$^1P - {}^1S$	0.533	0.562

Table 4 (Continued)

Ion	a	b	Transition	Hartree-Fock	Eq. (70)
N^{+2}	2	1	$^2P - {}^2D$	0.439	0.438
			$^2P - {}^2P$	0.436	0.424
			$^2P - {}^2S$	0.447	0.452
	1	2	$^4P - {}^4S$	0.425	0.435
			$^2D - {}^2D$	0.438	0.447
			$^2D - {}^2P$	0.441	0.454
			$^2P - {}^2D$	0.457	0.454
			$^2P - {}^2P$	0.462	0.461
			$^2S - {}^2P$	0.440	0.454
N^{+3}	2	0	$^1S - {}^1P$	0.374	0.359
	1	1	$^3P - {}^3P$	0.370	0.371
			$^1P - {}^1D$	0.387	0.384
			$^1P - {}^1S$	0.395	0.395
N^{+4}	1	0	$^2S - {}^2P$	0.323	0.320

Table 5

Values of the parameters appearing in (79)

N	Configurations* a	b	Transition	ζ(m)	α	β	γ	$\beta\gamma$	τ_α^1	τ_β^1
3	1	0	$^2S - {}^2P$	6	1	0	0	0	1.694	-
4	2	0	$^1S - {}^1P$	6	0.97432	0.22517	$-1/\sqrt{3}$	-0.13000	1.973	2.237
	1	1	$^3P - {}^3P$	18	1	0	0	0	2.066	-
			$^1P - {}^1D$	10	1	0	0	0	2.165	-
			$^1P - {}^1S$	6	-0.22517	0.97432	$-1/\sqrt{3}$	-0.56252	1.973	2.237
5	2	1	$^2P - {}^2D$	10	0.98633	0 16480	$-1/\sqrt{2}$	-0.11653	2.456	2.543
			$^2P - {}^2P$	18	0.98633	0.16480	$-1/\sqrt{2}$	-0.11653	2.366	2.595
			$^2P - {}^2S$	2	0.98633	0.16480	$\sqrt{2}$	+0.23306	2.527	2.543
5	1	2	$^4P - {}^4S$	12	1	0	0	0	2.437	-
			$^2D - {}^2D$	15	1	0	0	0	2.511	-
			$^2D - {}^2P$	10	-0.16480	0.98633	$-1/\sqrt{2}$	-0.69744	2.456	2.543
			$^2P - {}^2D$	15	1	0	0	0	2.563	-
			$^2P - {}^2P$	18	-0.16480	0.98633	$-1/\sqrt{2}$	-0.69744	2.366	2.595
			$^2S - {}^2P$	2	-0.16480	0.98633	$\sqrt{2}$	1.39488	2.527	2.543
6	2	2	$^3P - {}^3D$	15	0.99447	-0.10505	1	-0.10505	2.849	2.894
			$^3P - {}^3P$	9	0.99447	-0.10505	-1	0.10505	2.880	2.894
			$^3P - {}^3S$	12	0.99447	-0.10505	1	-0.10505	2.750	2.972
			$^1D - {}^1D$	15	0.99447	-0.10505	1	-0.10505	2.815	2.970
			$^1D - {}^1P$	5	0.99447	-0.10505	-1	0.10505	2.846	2.970
			$^1S - {}^1P$	4	0.97968	0.20054	-1	-0.20054	2.846	3.006

* $1s^2\ 2s^a\ 2p^b$, $1s^2\ 2s^{a-1}\ 2p^{b+1}$

Table 5 (Continued)

N	Configurations* a	b	Transition	ζ(m)	α	β	γ	$\beta\gamma$	τ_α^1	τ_β^1
	1	3	$^3D - {}^3P$	15	0.10505	0.99447	1	0.99447	2.849	2.894
			$^3P - {}^3P$	9	0.10505	0.99447	-1	-0.99447	2 880	2.894
			$^3S - {}^3P$	12	0.10505	0.99447	1	0.99447	2 750	2.972
			$^1D - {}^1D$	15	0.10505	0.99447	1	0 99447	2.815	2.970
			$^1P - {}^1D$	5	0.10505	0.99447	-1	-0.99447	2.846	2.970
			$^1P - {}^1S$	4	-0.20054	0.97968	-1	-0.97968	2.846	3.006
7	2	3	$^4S - {}^4P$	12	1	0	0	0	3.251	-
			$^2D - {}^2D$	15	1	0	0	0	3.260	-
			$^2D - {}^2P$	15	1	0	0	0	3.207	-
			$^2P - {}^2D$	5	0.99135	0.13125	$-\sqrt{2}$	-0.18562	3.260	3.327
			$^2P - {}^2P$	9	-0.13125	0.99135	$-\sqrt{2}$	-1.40198	3.207	3.379
			$^2S - {}^2P$	4	-0.13125	0.99135	$1/\sqrt{2}$	0.70099	3.296	3.327
8	2	4	$^3P - {}^3P$	18	1	0	0	0	3.663	-
			$^1D - {}^1P$	5	1	0	0	0	3.636	-
			$^1S - {}^1P$	2	0.98954	0.14427	$-\sqrt{3}$	-0.24988	3.636	3.775
	1	5	$^1P - {}^1S$	2	-0.14427	0.98954	$-\sqrt{3}$	-1.71393	3.636	3.775
9	2	5	$^2P - {}^2S$	6	1	0	0	0	4 065	-

* $1s^2\ 2s^a\ 2p^b$, $1s^2\ 2s^{a-1}\ 2p^{b+1}$

Table 6

Relative strengths of transitions

		Single Configuration				Double Configuration		
					$1s^2 2p^2$			
		^3P	^1D	^1S		^3P	^1D	^1S
$1s^2 2s2p$	^3P	18	-	-		18	-	-
	^1P	-	10	2		-	10	3.7
					$1s^2 2s2p^2$			
		^2D	^2P	^2S		^2D	^2P	^2S
$1s^2 2s^2 2p$	^2P	10	18	2		7.6	13.6	3.0
					$1s^2 2p^3$			
		^4S	^2D	^2P		^4S	^2D	^2P
	^4P	12	-	-		12	-	-
$1s^2 2s2p^2$	^2D	-	15	5		-	15	7.4
	^2P	-	15	9		-	15	13.4
	^2S	-	-	4		-	-	3.0
					$1s^2 2s^2 2p^2$			
		^3P	^1D	^1S		^3P	^1D	^1S
	^3D	15	-	-		11.9	-	-
	^3P	9	-	-		10.9	-	-
$1s^2 2s2p^3$	^3S	12	-	-		9.5	-	-
	^1D	-	15	-		-	11.9	-
	^1P	-	5	4		-	6.0	2.4
					$1s^2 2p^4$			
		^3P	^1D	^1S		^3P	^1D	^1S
	^3D	15	-	-		18.0	-	-
	^3P	9	-	-		7.1	-	-
$1s^2 2s2p^3$	^3S	12	-	-		14.5	-	-
	^1D	-	15	-		-	18.0	-
	^1P	-	5	4		-	4.0	5.6

Table 6 (Continued)

		Single Configuration				Double Configuration		
					$1s^2 2s^2 2p^3$			
		^4S	^2S	^2P		^4S	^2D	^2P
	^4P	12	-	-		12	-	-
	^2D	-	15	5		-	15	3.2
$1s^2 2s2p^4$	^2P	-	15	9		-	15	5.8
	^2S	-	-	4		-	-	4.7
					$1s^2 2s2p^4$			
		^2D	^2P	^2S		^2D	^2P	^2S
$1s^2 2p^5$	^2P	10	18	2		11.7_5	21.1_5	1.3
					$1s^2 2s^2 2p^4$			
		^3P	^1D	^1S		^3P	^1D	^1S
	^3P	18	-	-		18	-	-
$1s^2 2s2p^5$	^1P	-	5	2		-	5	1.1

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APPENDIX A

VALUES OF THE FIRST-ORDER MATRIX ELEMENTS

$$\langle V|Y_1^o(1s,1s)|v_o\rangle = -\frac{320\sqrt{3}}{3^6} \qquad (A.1)$$

$$\langle V|Y_1^o(1s,2s)|u_o\rangle = \frac{512\sqrt{3}}{3^9} \qquad (A.2)$$

$$\langle V|Y_1^o(2s,2s)|v_o\rangle = -\frac{111\sqrt{3}}{2^9} \qquad (A.3)$$

$$\langle V|Y_1^1(2s,2p)|w_o\rangle = -\frac{159\sqrt{3}}{2^9} \qquad (A.4)$$

$$\langle V|Y_1^o(2p,2p)|v_o\rangle = -\frac{143\sqrt{3}}{2^9} \qquad (A.5)$$

$$\langle v_o|Y_1^o(1s,2s)|v_o\rangle = \frac{512\sqrt{2}}{3^3 \times 5^5} \qquad (A.6)$$

$$\langle v_o|Y_1^1(1s,2p)|w_o\rangle = -\frac{256\sqrt{2}}{3 \times 5^5} \qquad (A.7)$$

$$\langle W|Y_1^o(1s,1s)|w_o\rangle = -\frac{560\sqrt{3}}{3^5} \qquad (A.8)$$

$$\langle W|Y_1^1(1s,2p)|u_o\rangle = -\frac{2624\sqrt{3}}{3^7} \qquad (A.9)$$

$$\langle W|Y_1^o(2s,2s)|w_o\rangle = -\frac{375\sqrt{3}}{2^9} \qquad (A.10)$$

$$\langle W|Y_1^1(2s,2p)|v_o\rangle = \frac{117\sqrt{3}}{2^9} \qquad (A.11)$$

$$\left\langle W \left| Y_1^o(2p,2p) \right| w_o \right\rangle = - \frac{535\sqrt{3}}{2^9} \qquad \text{(A.12)}$$

$$\left\langle W \left| Y_1^2(2p,2p) \right| w_o \right\rangle = - \frac{305\sqrt{3}}{2^9} \qquad \text{(A.13)}$$

$$\left\langle w_o \left| Y_1^o(1s,2s) \right| w_o \right\rangle = \frac{512\sqrt{2}}{3^3 \times 5^5} \qquad \text{(A.14)}$$

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